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(54) Title: COLORED METALLIC PIGMENTS		
(57) Abstract <p>The invention relates to a colored metallic pigment comprising the combination of metallic flakes and a polymer matrix encapsulating a solid colorant cured thereon.</p>		

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COLORED METALLIC PIGMENTSBACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates generally to the field of metallic pigments, and more particularly, relates to a process for preparing a colored metallic pigment suitable for use as a surface coating and to the colored metallic pigment product.

2. Discussion of the Prior Art

Metallic pigments in general, and aluminum pigments in particular are widely used in the coating industry to produce finishes of the type which have a metallic luster. The procedure generally used at the present time to produce a colored finish with a metallic luster is to disperse both a metallic pigment and a transparent colored pigment in a suitable vehicle. Such dispersions have achieved wide acceptance as automotive finishes wherein a plurality of interesting colors having a metallic luster have become increasingly popular.

In the past, attempts at coloring aluminum flake pigments have been tried by prior workers in the art, using a precipitation of iron oxide onto the aluminum pigment surface. This has produced a flake with a gold color, but the procedure has been rather complicated. Another process for coloring metallic pigments is disclosed in United States Patent No. 4,328,042 which teaches the vapor deposition of iron penta-carbonyl onto an aluminum flake surface. The subsequent oxidation of the iron penta-carbonyl to iron oxides and carbon dioxide then produces a colored flake. The color of this flake is dependent on the conditions of processing and thickness of the iron oxide layer. In United States Patent No. 4,158,074, a process for coloring aluminum powder is disclosed which comprises

immersing finely divided aluminum in a weak alkali solution containing a specified metallic salt and an aliphatic amine and then separating the aluminum from the solution. The need remains to provide a commercially acceptable procedure for economically coloring metallic pigments.

It is therefore an object of the present invention to provide a process for the preparation of colored metallic pigments, particularly aluminum pigments, wherein a surface coating can be produced having the desired metallic luster without requiring the additional dispersion of a transparent colored pigment.

It is a further object of this invention to provide a process to reproducibly and irreversibly color specific grades of aluminum flake pigments.

SUMMARY OF THE INVENTION

This invention relates to colored metallic pigments suitable for use as surface coatings, and more particularly, teaches how to make metallic particles having a color imparted thereto and wherein the desired metallic luster has been retained.

An experimental approach has been adopted for coloring metallic particles, such as aluminum flakes, with pigment particles encapsulated with polymers and copolymers. Such encapsulated pigment particles are of the type described and claimed in United States Patent No. 4,665,107 entitled "Pigment Encapsulated Latex Aqueous Colorant Dispersions". Such particles are hereinafter referred to as "PEL" colorants and can be obtained from Koh-I-Noor Rapidograph, Inc., Bloomsburg, New Jersey. The advantage of this approach is that the encapsulating polymer matrix can be designed specifically to interact directly with the metallic flake surface and result in good adhesion independent of the nature of the pigment particle.

The stability of colloidal dispersions, where all the dispersed particles are identical, may be brought about by coulombic repulsion where all the particles have the same ionic charge and hence are repelled by one another. Instability can occur when the particles have a very low charge or are oppositely charged. Selective interaction between two different types of dispersed particles require that the like particles are stable with respect to one another, so as to prevent flocculation, but that one type of particle will be unstable with another type. It is also expected from the theory of van der Waals attraction, which is a basic attraction which exists between all matter, that the attraction between a particle with a small radius of curvature, i.e., a colored pigment particle, and a flat particle, i.e., a metallic flake, will be greater than the attraction between two small particles. The theory suggests that it is possible for

both the colored pigment and the metallic pigment to have the same ionic charge, but that the charge on the colored pigment can be controlled so as to have a charge which is sufficiently high for stability between colored pigments, but low enough so as to be unstable with aluminum flakes.

This concept has been tested by measuring the electrophoretic mobility, which is a measure of the sign and magnitude of particle charge, of aluminum powder, 3A yellow PEL, and yellow pigment in water as a function of pH. The yellow pigment and the encapsulated pigment utilized in the PEL were Ciba Geigy YT-915-D Monastral Yellow. This experiment was carried out in water because the sign and magnitude of particle charge could be more conveniently controlled by pH. The results of these experiments show that all the particles are negative as a function of pH except for the aluminum which turned positive at pH values below 3. The yellow PEL and pigment were subsequently individually added to aluminum dispersions in water at the different pH values. The results were evaluated by observing the supernatant after sedimentation of the aluminum particles. A clear and colored supernatant were interpreted as effective and ineffective coloring respectively of the aluminum pigment.

The results showed that coloring of the aluminum particles occurred at a pH value of 2 for both PEL and yellow pigment where the aluminum was positive and the yellow PEL and pigment were negatively charged. Limited coloring was detected for the yellow pigment at pH of 4 where both the aluminum and the yellow pigment had a negative charge, but with a low value for the yellow pigment. Subsequent increases in pH for the colored aluminum pigment dispersions showed that the PEL remained with the aluminum particles while the yellow pigment slowly redispersed with modest agitation. These experiments indicated that initial coloring of aluminum pigments can be controlled by

surface charge, but that irreversibility of coloring requires additional adhesion brought about by the encapsulating polymer which may necessitate formulation for specific grades of aluminum pigments.

According to one embodiment of the invention there is provided a colored metallic pigment comprising the combination of metallic flakes and a polymer matrix encapsulating a solid colorant cured thereon.

Advantageously, the polymer and colorant comprise about 4% to 25% by weight of said combination.

Preferably, the amount of polymer to colorant is in a ratio of 10% polymer to 90% colorant to 90% polymer to 10% colorant.

Metallic flake material other than aluminum can be used, for example, zinc, brass, bronze, gold and the like.

The polymer matrix is formed preferably with a polymer selected from the group consisting of polyvinyl butyral resin, vinyl acetal polymers, bisphenol glycidyl ether type epoxy resin, rosin maleic copolymer resin, carboxyl functional acrylics, styrene/maleic anhydride copolymers and alkylated vinylpyrrolidone copolymers.

According to a further embodiment of the invention a coating composition is formed with the colored metallic pigment and suitable organic solvent. Preferably, the solvent comprises mineral spirits.

The invention also provides a method for preparing a colored metallic pigment comprising the steps of

A. Admixing metallic flakes in a lower alcohol,

B. Adding to the mixture of step A a colorant encapsulated in a polymeric matrix.

Preferably, the metallic flakes in said lower alcohol are at a concentration of less than 5%. Advantageously, the content of water is not more than 5%.

DESCRIPTION OF THE PREFERRED
EMBODIMENT OF THE INVENTION

The experimental conditions required for coloring metallic pigments with PEL must take into account three facts. One is that the PEL can only, in the practical sense, be supplied as aqueous dispersions. Another fact is that metallic pigments, such as aluminum pigments, are normally supplied as a paste in mineral spirits and must undergo minimum contact with water. The final fact is that water is only slightly soluble in mineral spirits. These facts require that the coloring procedure utilize an intermediate solvent which is mutually soluble in both water and mineral spirits since the presence of a second liquid phase will not permit direct interaction between the coloring particle and the metallic pigment. The general concept is that as the polarity of a molecule decreases, the solubility in water decreases and the solubility in mineral spirits increases. Alcohols of different chain length were evaluated as the intermediate solvent because of the wide range and systematic availability of the polarity of the alcohol series as a function of chain length, and because alcohols, in general, are economically available and are relatively safe in terms of environmental considerations.

The general laboratory procedure for coloring aluminum pigment was as follows. A known amount of commercial grade aluminum pigment, for example, Sparkle Silver 3000 AR Aluminum Paste, as manufactured and sold by Silberline Manufacturing Co., Inc., Homestown, Pennsylvania, the assignee of the present application, was added to 10 cc of alcohol in a test tube and shaken for about 30 seconds. A known amount of a 10% dispersion of PEL in water was then added to the aluminum pigment dispersion in alcohol and shaken intermittently for several minutes. The test tube was then allowed to stand for approximately two hours to

allow total sedimentation of the aluminum pigment. The clarity of the supernatant was then recorded along with the sedimentation height of the aluminum pigment. The sedimentation height is indicative of the packing density of the aluminum pigment which is a function of the degree of interaction between the aluminum particles. A clear supernatant indicated that either the PEL has colored the aluminum flakes and settled with the larger aluminum particles, or that the PEL particles have flocculated and settled as a result of the particle size of the flocculates. A colored supernatant, which can exhibit different degrees of color, indicated that the PEL particles were undergoing limited or no interaction with the aluminum flakes. The clarity of the supernatant was generally identified according to the three designations of clear, "C", partly clear, "PC", and unclear, "UC".

A series of experiments were typically conducted following the coloring step for the purpose of determining the irreversibility of the colored aluminum pigments in different solvents. The first experiment, which was necessary to remove most of the water in the system, was to decant the supernatant and to replace the supernatant with the pure solvent used in the coloring step. The aluminum pigment was again allowed to settle and observations were made concerning the clarity of the supernatant and the sedimentation height. This procedure was then repeated for mineral spirits, and for additional solvents such as n-butanol and toluene. The degree of coloring of the aluminum pigment was evaluated by making wire wound drawdowns on mylar film of the aluminum paste prepared in mineral spirits. The solvents employed preferably are low, water miscible alcohols, such as, for example, methanol, ethanol, propanol, isopropanol, 1-butanol and 2-butanol.

EXAMPLE 1

The initial experiments for the coloring of aluminum paste were carried out with the Sparkle Silver 3000 AR Aluminum Paste in the solvent n-butanol. N-butanol was employed inasmuch as it has a limited solubility for water of 10%, and is miscible with mineral spirits. The aluminum paste was first dispersed in the butanol and a yellow PEL, 3A, was subsequently added to the butanol and stirred for several minutes. Observation of the supernatant after sedimentation indicated that the aluminum particles were colored. The colored aluminum was then transferred to mineral spirits and drawdowns revealed that the aluminum particles were irreversibly colored with the yellow PEL under these conditions. The same treatment with the yellow pigment did not result in coloring of the aluminum pigment. Identical tests were run for a blue PEL with the same results.

EXAMPLE 2

A number of experiments were carried out to define the conditions necessary for coloring Sparkle Silver 3000 AR Aluminum Paste in n-butanol with the PEL dispersions. It was found that the degree of coloring the aluminum pigment was controlled primarily by the concentration of water in the butanol. Very little coloring was found to occur when the water concentration in the butanol exceeded 5%. One factor which had a pronounced effect on the degree of coloring of the aluminum pigment was the instability, i.e., the flocculation, of the PEL dispersions in butanol at the higher water concentrations. Since the PEL colorants are aqueous dispersions of about 10% solids, the aluminum pigment concentration in butanol had to be maintained below 5% in order to obtain good color value with a sufficient amount of PEL particles. The concentration of water in preparing the colored pigment can be controlled by evaporating water from the PEL formulation so that the PEL is increased in solids

concentration. Water can be directly added to the aluminum, PEL-alcohol slurry.

EXAMPLE 3

A series of different solvents, such as 2-butanol, tert-butanol, iso-propanol, n-propanol, and ethanol were evaluated as the intermediate coloring solvent. The objective was to evaluate the different solvents for efficient coloring at higher aluminum paste concentrations. The propanols were chosen as the primary solvents because they are good solvents for both water and mineral spirits, and, at least qualitatively, yielded the most consistent results in terms of color intensity. A systematic series of coloring experiments were carried out with n-propanol and isopropanol as the intermediate coloring solvent for a variety of PEL formulations as supplied by Koh-I-Noor, Rapidograph, Inc.

EXAMPLE 4

A blue and yellow PEL (5A) was used to color Sparkle Silver 3000 AR Aluminum Paste at different color levels in the range of 4% to 25% PEL solids based on aluminum paste in n-propanol at an aluminum paste concentration of 5%. The colored aluminum paste was subsequently transferred to mineral spirits and drawdowns of the resulting aluminum paste on mylar film was used to determine the relative color value. It was found that the color value increased with increasing PEL concentration up to 15% and leveled off at higher concentrations. Additional experiments in isopropanol with Silberline Manufacturing Co., Inc. Sparkle Silver 3000 AR Aluminum Paste and Tufflake TM 3645 Aluminum Paste for different PEL formulations as a function of the PEL concentration showed that greater color intensity could be obtained by increasing the PEL concentration above 25%, but that the degree of flocculation of the PEL tended to increase with increasing solids. This latter fact could present

problems for the stability of the colored aluminum pigment.

Scanning electron micrographs, SEM, were taken of the colored aluminum paste at PEL concentrations of 4% and 25%. Representative SEM results at high and low magnification for the high and low color levels are presented in Figures 1, 2, 3 and 4. The results show that the PEL is definitely attached to the aluminum flakes under conditions of coloring in n-propanol and subsequent transfer to mineral spirits. The results also indicate that a saturation concentration of PEL on the surface of the aluminum occurs which can be expected to be a function of the stability of the PEL dispersion at the time of coloring. The indication is that the degree of coloring is related to the surface charge of the PEL and aluminum, and that the degree of irreversibility of the PEL on aluminum is related to the properties of polymer present in the PEL formulation.

EXAMPLE 5

The conditions for coloring aluminum paste were evaluated for different experimental versions of PEL, and specifically for coloring Sparkle Silver 3000 AR and Tufflake 3645 Aluminum Pastes. The procedure adopted for evaluating the degree of coloring and the reversibility of the coloring was as follows.

The standard formulation was to disperse 0.5 g of aluminum paste in 10 cc of either n-propanol or isopropanol, and to add to the slurry 0.5 cc of PEL dispersions consisting of 6% to 10% solids. The mixture was then shaken in a test tube for one to two minutes and the aluminum flakes were allowed to settle. The turbidity of the supernatant and the sedimentation height of the aluminum was recorded. The supernatant was subsequently removed with a pipette and 10cc of fresh propanol was added followed by shaking and sedimentation. The sedimentation height and turbidity

of the supernatant were recorded followed by removal of the supernatant and the addition of 10cc of mineral spirits. A few drops of the resulting sediment were then placed on mylar film, the color value was observed, and the sedimentation height and turbidity of the supernatant were recorded. The color stability of the aluminum pigment was then evaluated in n-butanol and in some cases in toluene. Deviations from this standard procedure included variation of the concentration of aluminum paste and the PEL dispersion, and addition of different additives to the propanol during the first coloring step.

The results of the coloring tests are presented in Tables II-1, II-2 and II-3. The PEL used in these tests are presented in Table I. All of the results in Table II were carried out in a test tube with 10 cc of solvent. The columns in the Table II series are identified as follows. The first column identifies the grade and weight of aluminum paste. The second column identifies the grade and weight of PEL dispersion. The third column, which is headed by identification of the coloring solvent, identifies the sedimentation height in brackets and specifies the clarity of the supernatant, i.e., C-clear, PC-partly clear, and UC-unclear. This column also includes any additives used in the coloring step. The remaining columns, which are headed by identification of the rinse solvents, specify the sedimentation height and the clarity of the supernatant.

The results in Tables II-1, II-2 and II-3 summarize the coloring experiments which were carried out under different conditions with different PEL formulations for the Sparkle Silver 3000 AR and Tufflake 3645 Aluminum Pastes dispersed in n-propanol and isopropanol. The results in Table II are intended as a record for the evaluation of the different PEL dispersions and the experimental development for refining the conditions necessary for irreversible

coloring of aluminum pigment. Certain trends, however, were observed which led to additional experiments. The variables which were found to be important were the concentration and ratio of PEL to aluminum paste, and the concentrations of water and oleic acid dissolved in the propanol. The results in Table II, including the degree of coloring the drawdowns, also show that the different PEL formulations, which consists of different polymer combinations as the encapsulating material, color and irreversibly color both the Sparkle Silver 3000 AR and Tufflake 3645 aluminum pigments to different degrees. The results confirm that the Sparkle Silver 3000 AR and Tufflake 3645 aluminium pigments exhibit different surface properties, and have different sensitivities to the concentration of water and oleic acid in the propanol.

The colorants which can be used generally are any inorganic or organic pigments. Pigments which have been successfully employed include titanium dioxide, Sun Chemical Co. Sunfast Blue, American Hoechst Hostaperm Red, Chemical Co. Sunfast Green, Ciba-Geigy Irgazin Orange 5R, Ciba-Geigy Monastral Gold YT-915-D and Ciba-Geigy Monastral Gold YT-815-D.

EXAMPLE 6

The most consistent results, and the best color value and irreversibility of coloring was obtained for the ES2-3 series of PEL with isopropanol as the coloring intermediate solvent. In all cases the results indicate that water was a factor for controlling the color values on the aluminum pigment even when the supernatant of the coloring solvent was clear. This observation suggests that the concentration of water in isopropanol affects the stability of the PEL dispersions, where limited flocculation of PEL particles results in a loss of color value.

Observation of a large number of coloring experiments has shown that a clear supernatant in the

coloring step does not always result in significant coloring of the aluminum pigment. The interpretation of these data indicate that the mechanism for coloring is strongly dependent upon the stability of the DELPEL particles because flocculation of the PEL particles results in a clear supernatant and a loss of color value on the aluminum flakes. The stability of the DELPEL dispersions was, therefore, evaluated in n-propanol under different conditions and the results are summarized in Table III-1 through Table III-9. The first column in Table III identifies the grade and weight of the aluminum paste which was sedimented from 10 cc of the supernatant solvent, and the second column identifies the type and weight of the PEL dispersions added to the supernatant. The third and fourth columns in Table III-1 and Table III-2 give the stability results in the indicated solvents. The fifth column in Table III-1 and Table III-2 indicate whether or not the PEL particles would redisperse after sedimentation, which is an indication of the degree of stability of the particles. The third, fourth, and fifth columns in Tables III-3 to III-9 give the stability results for the indicated different concentrations of water added to the n-propanol. The stability results are expressed with the following notation: S-stable, PS-partly stable, SS-slightly stable, and US-unstable.

The concentration of the colorant can be varied from as little as 1% to as much as 99% based upon metal loading. Concentration averages in the range of from 10% to 30% colorant to 90% to 70% aluminum pigment have proved most satisfactory.

The interpretation of these data may be summarized as follows. All of the PEL particles appear to be more stable in n-propanol when water is present in the solvent. This appears to be due to the fact that polymer particles in general tend to undergo a change in charge as a function of concentration in the lower alcohols. This transition always results in a

region of instability due to low surface charge. The orange samples led to adequate coloring of the aluminum over a wide range of water concentration in propanol while the gold encapsulated PEL was found to require higher concentrations of water and in addition required a surfactant, i.e., sodium laurylsulphate. There is also an indication that the gold dispersion was undergoing a change in surface properties with time as evidenced by an increase in instability with aging time of the PEL dispersions. This instability leads to a loss in color value of the colored aluminum pigment possibly due to flocculation of the PEL particles on the surface of the aluminum flakes.

The PEL dispersion stability and coloring results indicated that the degree of interaction of the 3AXL27 PEL particles with the aluminum flakes in dispersed n-propanol is a function of the concentration of water in the propanol. The water concentration, furthermore, has potential of affecting the surface charge of the PEL particles and aluminum flakes. The electrophoretic mobility of Sparkle Silver 3000 AR and Tufflake 3645 Aluminum Pastes was measured in propanol as a function of water concentration in the range of 0% to 15%. The results show that the gold and orange samples are different and that both aluminum paste samples are negative at 0% water and are positive at 10% water. The different stability results for the Sparkle Silver 3000 AR and Tufflake 3645 Aluminum Pastes indicate that different grades of aluminum paste can exhibit different surface properties.

The mechanism proposed for the coloring of aluminum flakes is to generate a common condition for both the aluminum particles and PEL particles which results in stability of like particles, i.e., aluminum with aluminum and PEL with PEL, and instability with respect to unlike particles, i.e., PEL with aluminum particles. The different degrees of stability are proposed as being controlled by the surface charge of

the PEL and aluminum pigment particles. Coloring, therefore, can be expected to take place when the aluminum and PEL particles are oppositely charged or one of the particles, preferably the PEL particle, has at least a low charge. The parameters which appear to control the charge are the concentration and grade of the aluminum paste and the concentration of water in propanol. Experiments were carried out to investigate the electrophoretic mobility and stability of PEL dispersions in the supernatant obtained from different concentrations and grades of aluminum flakes in order to define the conditions present during coloring. These results were consistent with the results obtained from the coloring experiments. The objective of this line of research was to evaluate the conditions from maximum interaction of the PEL colorant with the aluminum flakes, and the relationship between these conditions and the reversibility of the coloring process.

The major experimental effort was carried out with earlier formulations of PEL dispersions which generally were effective for coloring the Sparkle Silver 3000 AR and Tufflake 3645 Aluminum Paste grades but which showed some problems with respect to shelf life and irreversible coloring in different solvents. The more recent ES2-3 PEL formulation shows improvements in all respects including coloring characteristics with different color pigments. The indication, however, is that this PEL colors Tufflake 3645 Aluminum Paste more efficiently than the Sparkle Silver 3000 AR Aluminum Paste.

It has been found that other materials, such as mica, can be successfully colored by employing the above coloring techniques. 15.0g of white mica, - 325 mesh wet ground was dispersed in 45.0g isopropanol and 50.0g PEL and 0.03g Epicure 874 were added. All components were slurried and then allowed to react. The colored material was collected and the results

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WHAT IS CLAIMED IS:

1. A colored pigment comprising the combination of flakes and a polymer matrix encapsulating a solid colorant cured thereon.
2. The colored pigment of claim 1 wherein the flakes are metallic flakes.
3. The colored pigment of claim 2 wherein the metallic flakes comprise aluminum flakes.
4. The pigment of claim 2 wherein said polymer and colorant comprise about 4% to 25% by weight of said combination.
5. The pigment of claim 2 wherein said polymer and the colorant is in a ratio from 10% polymer to 90% colorant to 90% polymer to 10% colorant.
6. The pigment of claim 3 wherein said polymer and colorant comprise about 4% to 25% by weight of said combination.
7. The pigment of claim 3 wherein said polymer and said colorant is in a ratio from 10% polymer to 90% colorant to 90% polymer to 10% colorant.
8. The pigment of claim 2 wherein said metallic flakes comprise zinc.
9. The colored pigment of claim 2 wherein the flakes are selected from the group comprising zinc, brass, bronze and gold flakes.
10. The colored pigment of claim 1 wherein the flakes are mica flakes.
11. The pigment of claim 1 wherein said polymer is selected from the group consisting of polyvinyl butyral resin, vinyl acetal polymers, butyrals, bisphenol glycidyl ether type epoxy resin, rosin maleic copolymer resin, carboxyl functional acrylics, styrene/maleic anhydride copolymers and alkylated vinylpyrrolidone copolymers.
12. A coating composition comprising the pigment of claim 1 and a suitable organic solvent.
13. A coating composition comprising the pigment of claim 3 and a suitable organic solvent.

14. The coating composition of claim 13 wherein said solvent comprises mineral spirits.

15. A method for preparing a colored metallic pigment comprising the steps of

A. admixing metallic flakes in a lower alcohol, and

B. adding to the mixture of Step A a colorant encapsulated in a polymeric matrix.

16. The method of claim 15 wherein said metallic flakes in said lower alcohol are at a concentration of less than 5% by weight.

17. The method of claim 15 wherein the content of water is not more than 5% by weight.

18. The method of claim 15 wherein the resulting colored metallic pigment is separated from said admixture with mineral spirits.

19. The method of preparing a colored metallic pigment comprising the steps of

A. admixing aluminum flakes in mineral spirits;

B. dispersing the aluminum flake and mineral spirit mixture in a low, water miscible alcohol;

C. adding a colored PEL; and

D. coloring the aluminum flakes.

20. The method of claim 19 and transferring the colored aluminum flakes to mineral spirits.

21. The method of claim 19 comprising the step of maintaining the concentration of aluminum flakes and mineral spirits in the alcohol below 5% by weight.

22. The method of claim 19 wherein the colored PEL comprises between about 6% to about 10% solids dispersed in water.



FIG. 2

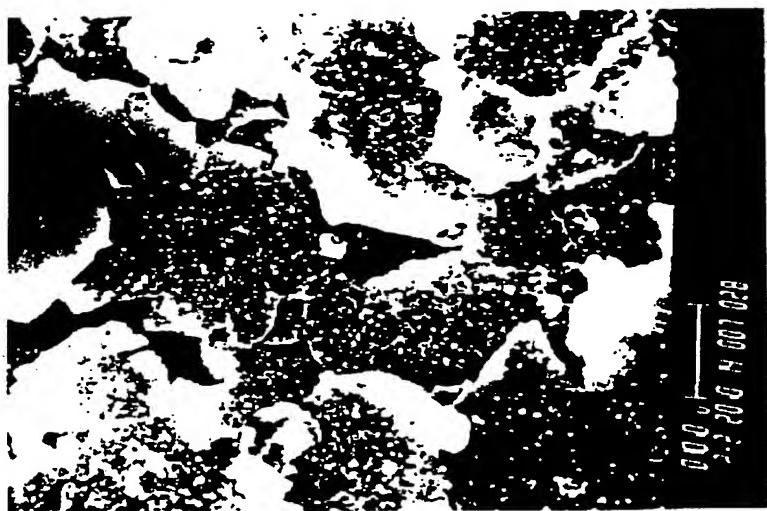


FIG. 1

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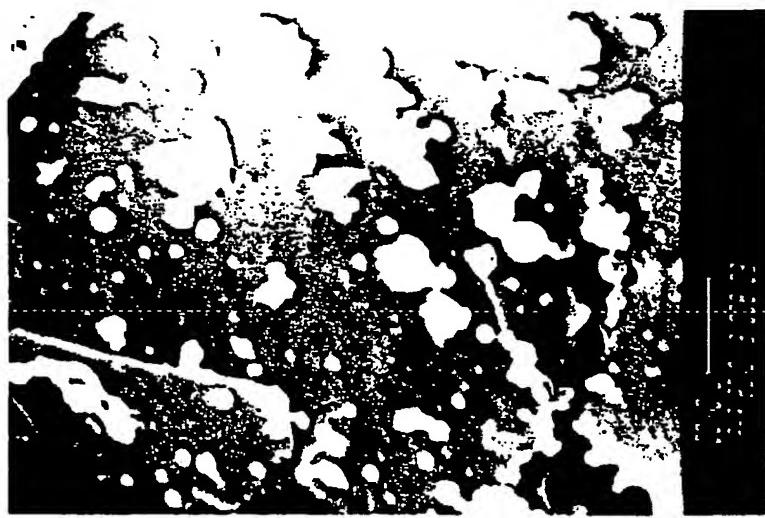


FIG. 4

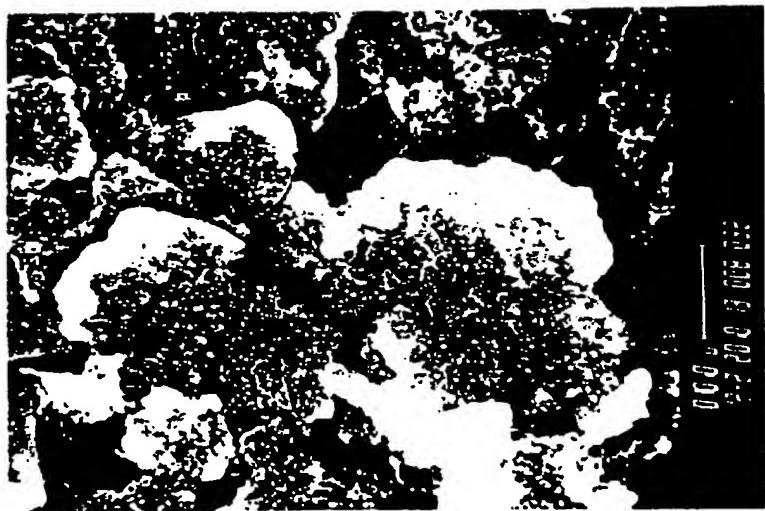


FIG. 3

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/05236

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5): C08K 5/34, 5/13
 U.S. CL. 523/207, 210; 106/417, 491

II. FIELDS SEARCHED

Minimum Documentation Searched?

Classification System	Classification Symbols
U.S.	523/207, 210; 106/417, 491

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Description of Document, ** with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. ****
A	US, A, 2,017,156 (BAER) 16 FEBRUARY 1937	1, 15, 19
A	US, A, 4,328,042 (OSTERTAG) 04 MAY 1982	1, 15, 19
A	US, A, 4,158,074 (UCHIYAMA ET AL) 12 JUNE 1979	1, 15, 19
A	US, A, 3,026,220 (SOWARDS) 20 MARCH 1962	1, 15, 19
A	US, A, 4,395,499 (ROSENSKI ET AL) 26 JULY 1983	1 & 15
A	US, A, 3,932,320 (CAMELON ET AL) 13 JANUARY 1976	1 & 15
A	US, A, 4,188,236 (ROBERTSON ET AL) 12 FEBRUARY 1980	1 & 15
A	US, A, 4,738,892 (CANOVA) 19 APRIL 1988	1 & 15
A	US, A, 3,656,981 (BESCHKE ET AL) 18 APRIL 1972	15 & 19
A	US, A, 3,876,603 (MAKHLIOUF) 08 APRIL 1975	1, 15, 19

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the International filing date
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 "P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

08 NOVEMBER 1990

Date of Mailing of the International Search Report

28 JAN 1991

International Searching Authority

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Signature of Authorized Officer

Christopher Rogers

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 3,451,835 (GANTER ET AL) 24 JUNE 1969	1, 15, 19
A	US, A, 3,843,571, (FITZGERALD) 22 OCTOBER 1974	1, 15, 19
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